PHOTOIONIZATION OF TMPD IN SOLUTION OBSERVED BY FEMTOSECOND TIME RESOLVED ABSORPTION SPECTROSCOPY

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We have studied the photoionization in solution of the aromatic amine N,N,N',N'-tetramethyl-p-phenylenediamine (TMPD) in solvents of diverse polarities. Our results characterize the spectral dynamics during the first few picoseconds following monophotonic excitation with 265nm, 100fs pulses using a continuum probe pulse. The 265nm excitation energy (4.7 eV) corresponds to the $S_2$ absorption band of TMPD and is below the known gas phase ionization threshold (6.5 eV). As will be discussed, the early evolution of the absorption bands assigned to the $S_1$ to $S_n$ transition and the radical cation of TMPD provide insight into the role of the solvent in the formation of ions from vibronically unrelaxed species under our experimental conditions.